REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
27-04-2015	Final Report	12-Feb-2014 - 11-Feb-2015

4. TITLE AND SUBTITLE
Final Report: Acquisition of Raman Spectrometer and High Temperature & Pressure Reactor for Synthesis and Characterization of Carbon Based Hybrid Nanoparticles from Waste Wood

5a. CONTRACT NUMBER
W911NF-14-1-0091

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
206022

6. AUTHORS
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
64754-MS-REP.1

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
We have purchased four instruments using this grant, including a custom built high temperature pressure reactor from Parr Instruments, DXR-Raman spectrometer (Thermoscientific), BET surface area measurement system (NOVA-2200e) from Quantachrome and high temperature pressure hydrothermal reactor (RC-Ni100, MTI corporation). These tools were fully installed and operational. We have also synthesized carbon materials from waste biomass using these two high temperature reactors. We have extensively used a Raman spectrometer to

15. SUBJECT TERMS
Acquisition, Raman Spectrometer, High temperature & pressure reactor, carbon nanoparticles, waste wood

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
UU	UU	UU	UU		Vijaya Rangari
					19b. TELEPHONE NUMBER 334-724-4875

Report Title

Final Report: Acquisition of Raman Spectrometer and High Temperature & Pressure Reactor for Synthesis and Characterization of Carbon Based Hybrid Nanoparticles from Waste Wood

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We have purchased four instruments using this grant, including a custom built high temperature pressure reactor from Parr Instruments, DXR-Raman spectrometer (Thermoscientific), BET surface area measurement system (NOVA-2200e) from Quantachrome and high temperature pressure hydrothermal reactor (RC-Ni100, MTI corporation). These tools were fully installed and operational. We have also synthesized carbon materials from waste biomass using these two high temperature reactors. We have extensively used a Raman spectrometer to analyse as synthesized carbon materials. We have also measured surface area of these carbon materials using BET surface area analyzer. The initial results are very encouraging and we contine exploring these systems to produce carbon materials from various biowaste we have also extended this carbonization to electronic waste material. The analytical tools procured from this grant are incorporated into the graduate level materials characterization course (MSEG-604) and also Nanoscale Science and Engineering course (MSEG-612).

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Dr.Rangari received a Tuskegee University Faculty Achievement award for 2014-2015

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
No person support is requested	0.00	
Boniface Tiimob	0.00	
Hannah Harding	0.00	
Samia Islam	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**4**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME	
Vijaya Rangari	
Total Number:	**1**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

None

Acquisition of Raman Spectrometer and High temperature & pressure reactor for synthesis and characterization of carbon based hybrid nanoparticles from waste wood

Abstract:

We have purchased four instruments using this grant, including a custom built high temperature pressure reactor from Parr Instruments, DXR-Raman spectrometer (Thermoscientific), BET surface area measurement system (NOVA-2200e) from Quantachrome and high temperature pressure hydrothermal reactor (RC-Ni100, MTI corporation). These tools were fully installed and operational. We have also synthesized carbon materials from waste biomass using these two high temperature reactors. We have extensively used a Raman spectrometer to analyse as synthesized carbon materials. We have also measured surface area of these carbon materials using BET surface area analyzer. The initial results are very encouraging and we contine exploring these systems to produce carbon materials from various biowaste we have also extended this carbonization to electronic waste material. The analytical tools procured from this grant are incorporated into the graduate level materials characterization course (MSEG-604) and also Nanoscale Science and Engineering course (MSEG-612).

Using this grant, we have procured following four pieces of instruments:

1. **Custom built High temperature/pressure reactor (Parr instruments):**

Figure 1 High Temperature/pressure reactor

This equipment is designed such a way that the reactions can take place at ~2000 psi pressure and ~800^{o}C temperature. The reaction vessel capacity is about ~35mL.

2. **DXR Raman Spectrometer (Thermoscientific):**

Figure 2 Raman microscope for molecular spectroscopic characterization of materials

This Raman spectrometer is configured with two lasers (532nm, 780nm) and three objective lenses (10X, 50X, 100X), with a high precision motorized microscope stage.

3. **BET surface area, Nova 2200e (Quantachrome)**

Figure 3 BET surface area analyzer for material characterization

This BET surface area analyser is configured with one sample and two samples preparation stages.

4. **Custom build high temperature/pressure hydrothermal reactor (MTI corporation)**

Figure 4: High temperature/pressure hydrothermal reactor

This hydrothermal reactor is capable of reacting ~100ml of materials at pressure of ~2000 psi pressure and 1100^{o}C temperature. This equipment is installed in Dual Explosion-Proof Box for safety.

Using above instruments we have synthesized and characterized various materials and the results are as follows:

1. **Synthesis and characterization of coconut shell derived resource carbon material**

What we hear and see as the days roll out suggest that the world is drifting into a future where every material regarded as waste must be consumed in such a way that it will lead to benefits in the society. Resources continue to be scarce [1] and depleted daily, and the fundamental rhetorical questions about the plight of the generation in the next century continue to linger in the minds of the conservationist, stakeholders and policy makers involved in such issues and as well as in climate change. The urgent for interventions on these growing issues motivate us to immediately seek solutions to avert this ameliorating situation. It is in the light of this that we want to contribute in the area of sustainable and renewable material development. In this work, we are exploring the conversion of renewable waste amorphous material (coconut shell) into semi crystalline carbon materials with tailored properties suitable for applications in the design of low-cost filter, energy and structural materials [2, 3, 4]. Approximately 10 grams of > 150 µm coconut shell powder (CSP) was heated in a high pressure reactor shown in figure 1 (Parr 4838) at 5 ˚C/min to 800 ˚C. This was held isothermally at 800 ˚C for 2 hours under autogenic Isobaric pressure of 124 bars (1800 psi) emanating from the combustion of the CSP in one set of experiment whiles in another the pressure was released. A yield of approximately 3 grams was obtained in both cases. These two carbonized materials were divided into three (about 1 gram each) into a 20 mL aluminum oxide crucible and microwaved (Microwave Research and Applications Inc.) at 50 µP for 15, 30 and 60 minutes at 1100 ˚C. The specimens were characterized using multipoint BET surface area measurement and Raman microscopy.

The surface areas measured by a 11 point BET analysis of the coconut shell derived carbon materials are presented in table 1. These revealed increases in surface areas in both cases due to the microwave heating but this is significant at 15 and 30 minutes heating of the 0 pressure specimen. Also the autogenic pressure showed significant influence on the carbonized material which was not microwave heated, in that, the surface area is ~238 fold more. These preliminary results show the surface area is higher than those reported for birch wood derived porous carbon [5] and great promise for further research.

Table 1. BET surface areas of coconut shell carbon materials

Specimen	**Microwave Time (min)**	**BET surface Area (m^2/g)**	
		0 pressure	**124 bars**
CSP	-	0.4	95.1
CSP-15	15	417.7	242.4
CSP-30	30	832.3	286.5
CSP-60	60	77.2	165.3

Raman spectroscopy is a very powerful technique for characterizing carbon based materials such as graphene its derivatives like graphene-oxide. Figure 5 shows the Raman spectra of the raw cellulosic coconut shell powder as received and those of its derived materials processed through autogenic high pressure reaction and microwave irradiation.

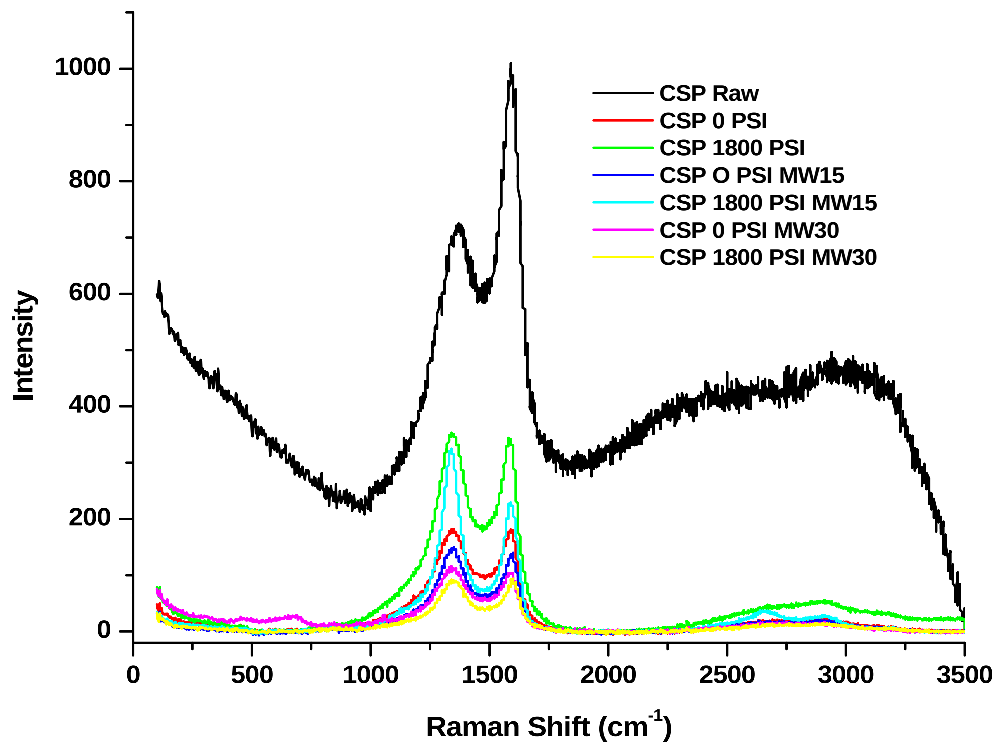

Figure 5 Raman spectra of coconut shell based carbon materials

The spectra show the typical disordered (D) and graphite (G) bands found in most carbon materials due to Raman vibrational excitations. The D band occurs at 1350cm^{-1} while the G is at 2700^{-1}, suggests the formation of very small crystallites of graphene-oxide from the coconut shell powder. This is very significant because graphene oxide can be used for making graphitic polymer composites which retains some of the electrical properties of graphene while maintaining the physical properties of the polymer.

2. Raman microscopy of biodegradable polymer blends and egg proteins

The need for compostable alternative packaging materials is an urgent one, due to the continuous inevitable demand in copious quantities by the ever increasing consumer population. Unfortunately, the mostly used polymeric packaging materials are still recalcitrant to degradation, and contribute significantly to climate change issues now confronting the world. Increasing volumes of synthetic polymers are manufactured and used for various applications, mostly for packaging materials. Disposal of the used polymers has been accumulated under the land surface and remain there for several years. Unlike natural polymers, most synthetic polymers cannot be decomposed by microorganisms, hence the landfill approach becomes inefficient, and other plastics waste management should be found. A study of the biodegradation properties of synthetic polymers has become very important. This is because the development of compostable substitutes will immensely help in curtailing the issues related to the environmental waste and climate change. In this research, we study the fabrication and molecular characteristics of compostable poly (butylene adipate-co-terephthalate) (PBAT)/agro-based polylactic acid (PLA) blend films using single screw extrusion process. The polymer blends of PBAT/PLA (90/10, 80/20, 70/30, 60/40 and 50/50) were extruded and characterized using dispersive Raman microscope shown in figure 6.

Figure 6 show the Raman spectra for the two virgin polymers and those of 70/30 and 50/50 blends. The Stokes phonon energy shift caused by laser (532 nm) excitation creates several peaks on the Raman spectrum of each polymer system. As evident in figure 6, the spectra pattern for each neat system is unique and different from those of the blends.

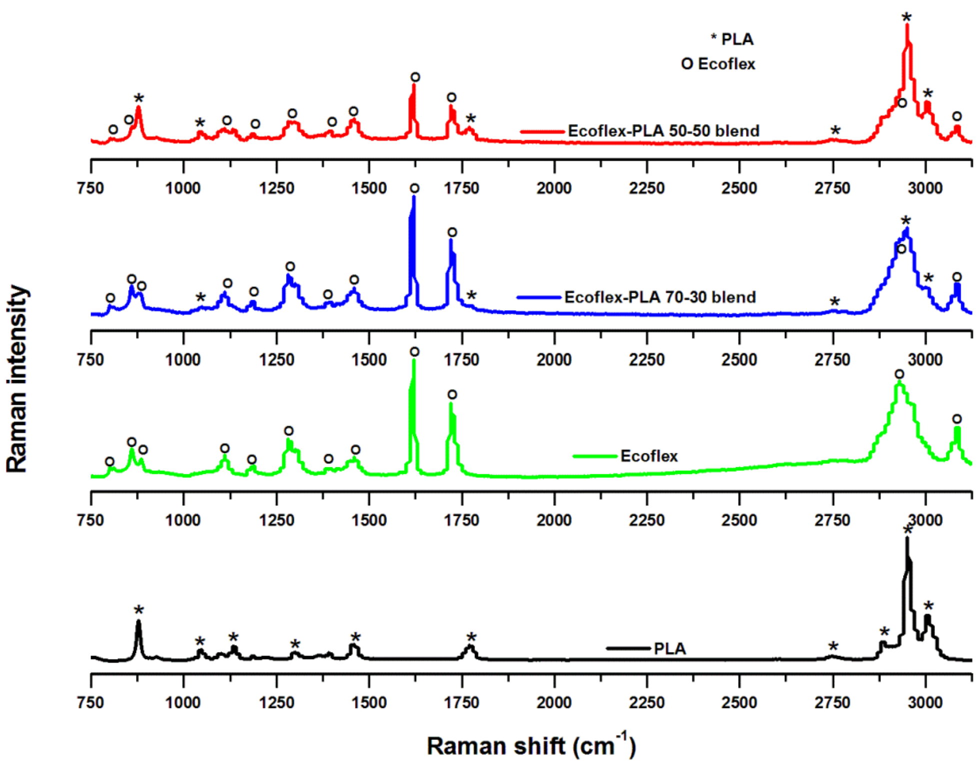

Figure 6 Raman spectra of the neat and blended polymer systems

However, the patterns for the blends are similar and show peaks from both polymers blended. The signature (unique chemical groups) of each polymer has been identified in the blends and marked as shown in the 70/30 and 50/50 miscible blends in the figure.

Also, the protein films on the inner layer of raw and boiled eggshells were characterized by the Raman spectroscopy to help investigate the effect of temperature on the eggshell proteins. Some functional groups on the eggshell due to the proteins are relevant to the applications of eggshell derived materials which are heat treated and this investigation will help in the understanding and modification of processing method to avoid protein denature in the eggshell. Figure 7 show the Raman spectra of egg protein film subjected to 30 minutes of boiling and that of a raw egg film. The spectra generally do not show any distinction in the peak position but does show reduced peak intensities in the boiled protein film. This suggests that the proteins are not denatured in the boiled egg shell.

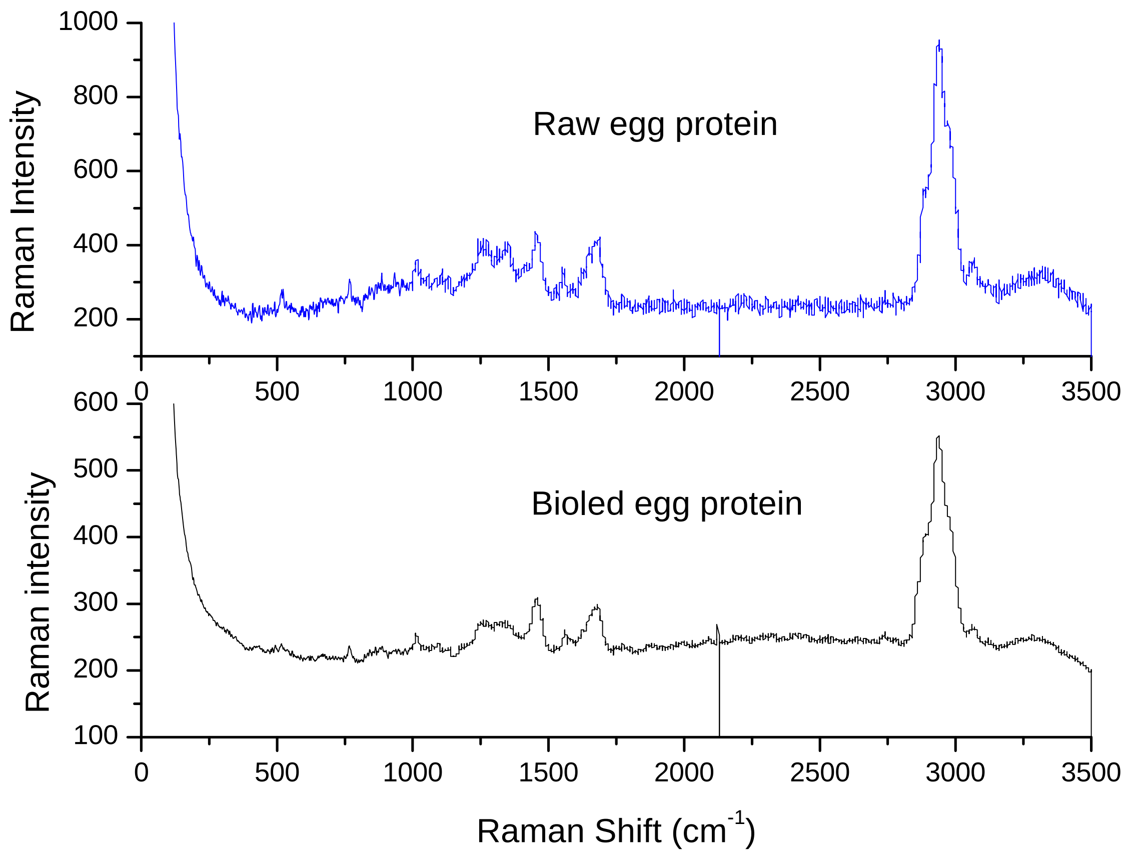

Figure 7 Raman analysis of boiled and raw eggshell proteins

3. Synthesis of Silica from agricultural waste such as Rice husk and Sugar bagasse using high temperature pressure reactor

Rice Husk (RHs) and Bagasse (BG) are good sources of bio based Silica (SiO_2), which derive from different agro industries as a bio waste. USA alone produced 279,000 billion ton sugar cane and 90,482 billion ton of rice/paddy in the year of 2012 [6] RHs and BG are by product of rice and sugar cane, contributing almost 20-22% weight of the total rice and sugar production. Usually, this huge amount of bio waste is used very ineffectively, such as for rural energy production in fire stoves or sometimes for making fire in brick production. Although these are some way to utilize this bio-mass, it leads to a waste of some engineering ceramic products that come out from this bio-mass the Silica. These bio-masses have a high percentage of silica content (above 90%). Highly crystalline SiO_2 from RHs, and BG can be utilized for different engineering purposes. The Bio based SiO_2 can replace the Synthetic SiO_2 for various applications. The production of synthetic SiO_2 is a complex industrial process. It involves high energy consumptions for pure SiO_2 production. On the other hand, bio based SiO_2 production from RHs, and BG is a very simple Autogenic pressure process. The bio based SiO_2 can be easily used in a wide range of applications, from reinforcement to element in semiconductor industries.

For this study the Rice husk was procured from Three H's, LLC Crossett, Arkansas, a US based paddy industry. RH was then ball milled for 20 minutes to produce a powder of RH and then used for extraction of RH silica. Rice husks powder was pyrolysed at 800°C and further burned in a tube furnace under open atmosphere. Synthesis of Rice Husk silica is illustrated in figure 8 and 9. Figure 8 presents the overall methodology to get silica from the raw rice husk. On the other hand, figure 9 represents a step by step image of silica processing.

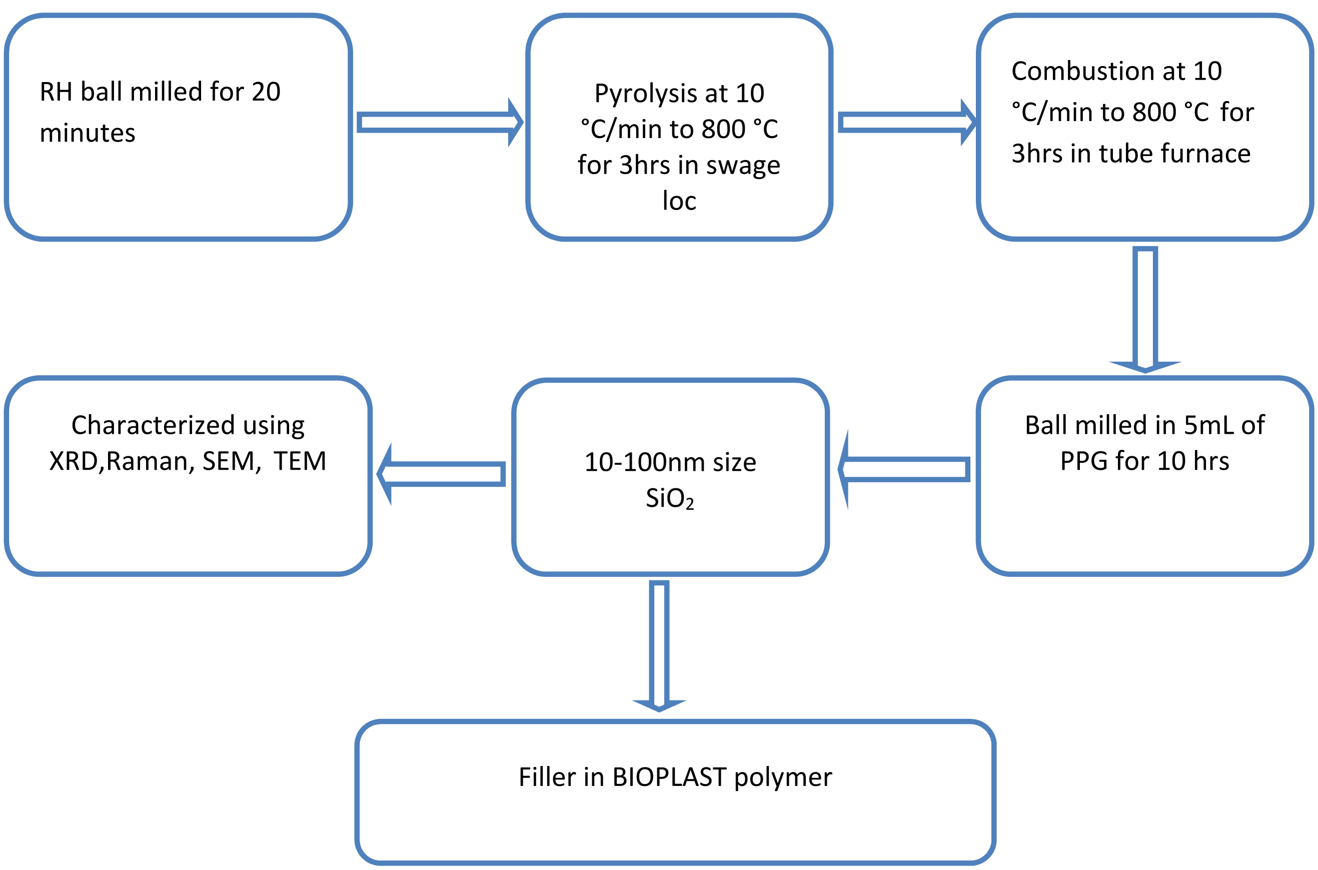

Figure 8. Synthesis of Silica from Rice Husks.

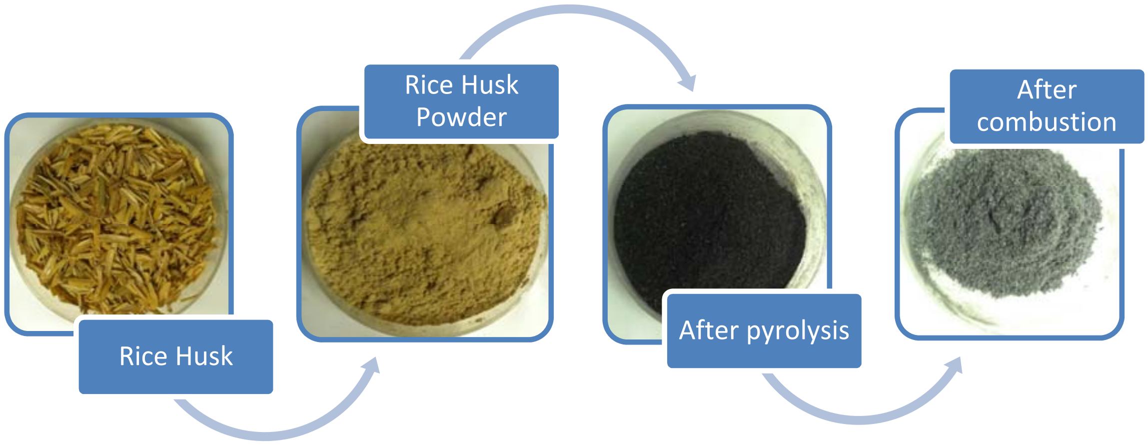

Figure 9. Synthesis of Silica from Rice Husks.

Since the crystalline silica is Raman active we have studied the crystalline structural behaviour of synthesized particles. Crystalline silica (RHs, and BG) has been studied using Raman spectroscopy to confirm the crystalline structure and type of silica. The characteristic wave length of bagasse (Quartz) 465cm^{-1} and 200 cm^{-1} confirm the quartz structure of silica. These results are consistent with the library data base and also the literature [7]. Cristobalite also identified with the help of Raman library file which matches with the significant 240 cm^{-1} and 421 cm^{-1} wave length. This one also conforms to the literature.

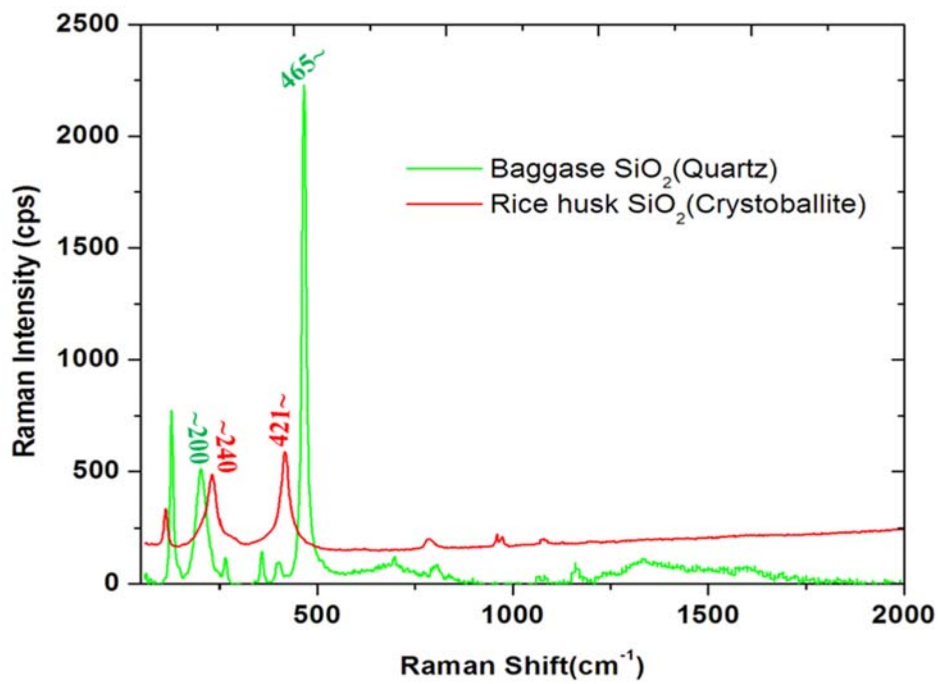

Figure 10. Raman spectra of Bagasse (Green spectra) and Rice Husk (Red spectra) silica.

4. **Synthesis and surface area characterization carbon from recovered electronic waste as a potential polymer filler**

The hype in usage of electronics leads to the generation of a commensurate high quantity of electronic wastes competing for space in the landfills. Instead of disposing off these recalcitrant electronic materials, they can be recovered through sustainable techniques and used in other beneficial ways. This dimension of the research focuses on the development of carbon based materials from electronic waste for energy generation and polymer additive applications. Preliminary work carried out using a high temperature/pressure reactions and ball milling techniques to recover carbon material from computer casing polymer. BET surface area analysis was conducted on this material and a number of different carbon materials obtained through different synthesis routes to enable us tune our procedure. BET surface and pore size analyzer in figure 3 by Quantachrome Instruments was used in the analysis.

The samples were degassed at 300°C for 3h under Helium. The samples were run under liquid nitrogen and the BET was calculated. The BET surface area measurements for the different carbon specimens are shown in figure 11.

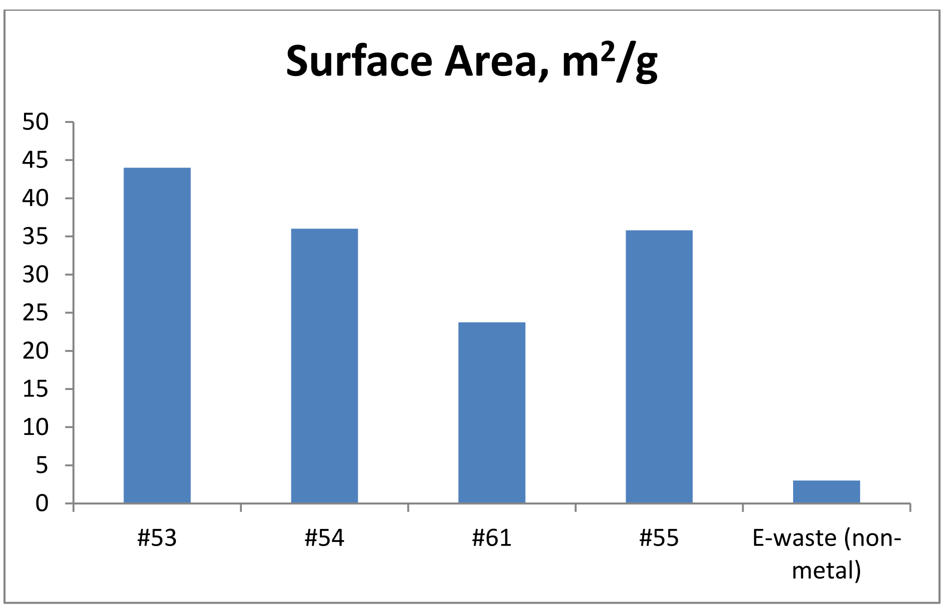

Figure 11. BET surface areas of carbon materials

5. Surface morphogical characteristic of eggshell and its derived inorganic additive material

The Avian eggshell is a cheap and endowed source of calcium carbonate which can be used for polymer additive applications, tissue regeneration, micronutrient supplement, drug delivery and a precursor for the synthesis of other calcium based functional inorganic materials. The functionality and reactivity of these materials depend very much on their size and morphology. Hence BET surface analysis of such materials contributes significantly toward the development of a more functional material for a specific application. We have analyzed the surface areas of micron and nano eggshell sourced calcite crystals as well as hydroxyapatite nucleated from digested eggshell precursor to enable the assessment of particle size dependent enhancement of these materials when used as polymer additives. These are presented in table 2.

Table 2 Surface areas of bio source inorganic functional materials

Material	**BET Surface area (m/g^2)**
Micron eggshell	1.16
Nano eggshell	10.45
Hydroxyapatite	95.92

The results in table indicate that the surface area of the nano eggshell is about ten times more than its micron counterpart but that of the hydroxyapatite is almost hundred times. This is promising and suggests that surface properties of these materials can be tailored to a desired application with further experimentation. Each of these sizes has different aspect ratio and will affect the functionality accordingly. In polymer matrix, high surface areas can lead to drastic improvement in mechanical properties.

The analytical tools procured from this grant are incorporated into the graduate level materials characterization course (MSEG-604) and also Nanoscale Science and Engineering course (MSEG-612).

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